

Sampling methods which require indirect knowledge of parameters that are difficult to quantify should be avoided. The gas tracer method has been used with at least partial success, but applications do not yet appear widespread. When stream reaeration rates are being measured the wind should be light or calm; otherwise wind effects can produce atypical reaeration rates.

In deep, slowly moving backwater regions of rivers reaeration can either be simulated using a river formula or lake formula. The O'Connor-Dobbins method is probably the most appropriate stream formula to use, although for very slowly moving backwater regions the predicted reaeration coefficient can be between 0.01 to 0.05/day, which is below the range of k_2 values used in the development of the formula. If a lake reaeration formula is used, the reaeration rate coefficient can exceed the range predicted using the O'Connor-Dobbins formula. Under these conditions, wind and not depth and velocity can control the rate of reaeration.

3.3 CARBONACEOUS DEOXYGENATION

3.3.1 Introduction

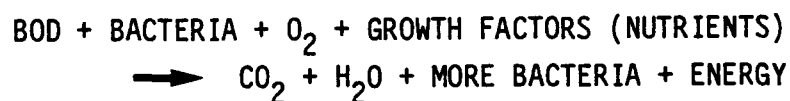
Biochemical oxygen demand (BOD) is the utilization of dissolved oxygen by aquatic microbes to metabolize organic matter, oxidize reduced nitrogen, and oxidize reduced mineral species such as ferrous iron. The term BOD is also applied to the substrate itself. Concentrations of reduced minerals in waste streams are usually inconsequential, and so BOD is commonly divided into two fractions: that exerted by carbonaceous matter (CBOD) and that exerted by nitrogenous matter (NBOD). In domestic wastewaters, CBOD is typically exerted before NBOD, giving rise to the well-known two-stage BOD curve (although the processes can be simultaneous in natural systems and certain industrial effluents). Because wastewaters are potentially high in BOD, and because dissolved oxygen concentration is used as a principal determinant of the health of an aquatic system, BOD is a widely applied measure of aquatic pollution. This section discusses dissolved and

suspended CBOD; Section 3.4 deals with NBOD and Section 3.5 treats benthic oxygen demand or sediment oxygen demand (SOD). All are related processes.

Figure 3-10 shows the major sources and sinks of carbonaceous BOD in natural waters. Anthropogenic inputs include point sources and nonpoint sources such as urban runoff and feedlot runoff. Autochthonous sources derived from the aquatic biota (particularly algae) can be important in some systems. Also, re-entrainment of oxygen-demanding material from benthic deposits may occur. Removal of CBOD from the water column occurs through sedimentation, microbial degradation and the sorption to or uptake by the benthic flora. Some components of BOD may also volatilize from the water column. Carbonaceous material which has settled or been sorbed becomes part of the benthic oxygen demand.

It is important that the analyst distinguish in the modeling process between both the sources of BOD and the instream removal mechanisms. Waste load allocation decisions based upon models which consider CBOD as a "lumped" quantity may not accurately or fairly assess the water quality impact of the point sources.

Efforts to characterize CBOD kinetics have focused chiefly on water-column decay processes, and that is the major emphasis of this section. A general expression for BOD decay is:



3.3.2 Water Quality Modeling Needs

Nearly all water quality models characterize CBOD decay with first order kinetics represented by:

$$\frac{dL}{dt} = -k_d L \quad (3-26)$$

where L = ultimate CBOD, mg/l

k_d = first order rate coefficient, 1/day, base e

t = time, days

This equation when coupled with stream dissolved oxygen kinetics becomes the classic Streeter-Phelps equation:

$$D = \frac{k_d L}{k_2 - k_d} \left[e^{-k_d t} - e^{-k_2 t} \right] + D_0 e^{-k_2 t} \quad (3-27)$$

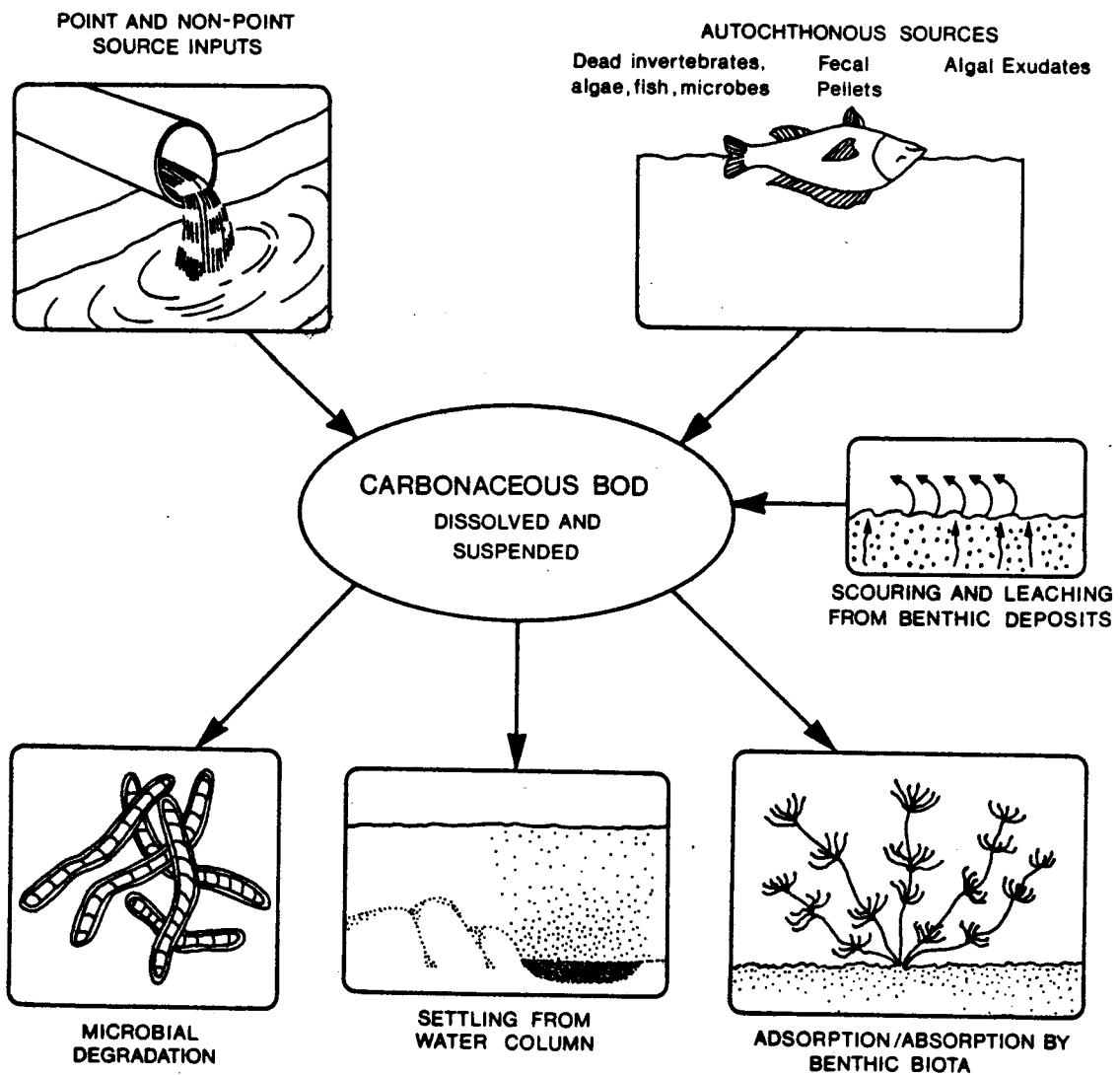


Figure 3-10. Sources and sinks of carbonaceous BOD in the aquatic environment.

where D = dissolved oxygen deficit, mg/l

k_2 = stream reaeration rate, 1/day, base e

D_0 = initial stream deficit, mg/l

This equation in principle is similar in nearly all state-of-the-art water quality models.

In using this representation of BOD/DO for waste load allocation modeling, the analyst may require measurement or estimation of three independent factors which include:

- (a) the magnitude of ultimate CBOD of the point sources and the resulting instream spatial distribution,
- (b) the magnitude and spatial distribution of the instream CBOD removal rate, and
- (c) the ratio of point source ultimate CBOD to 5-day CBOD (if compliance is to be based upon $CBOD_5$).

It is important to note that the water quality model is based upon ultimate CBOD and not $CBOD_5$. Some models internally convert from 5 day to ultimate using an assumed ratio. In the case of the QUAL-II model (NCASI, 1982a), this ratio is 1.46 and is not user specified. This assumption has significant implications to water quality modeling because recent experience has shown that this ratio is both wasteload and receiving water specific. Ultimate to 5 day ratios as high as 30 have been reported for some paper industry wastewaters (NCASI, 1982d). Since first order kinetics are assumed in most models, the ultimate to 5 day ratio is not independent of the decay rate, k_d . Consequently, analysts should be certain that the river water ultimate to 5 day BOD is not assigned independently of the rate, k_d .

3.3.3 Nomenclature

Since microbial degradation is not the only process contributing to the observed depletion of CBOD in a water body (see Figure 3-10), laboratory rates of carbonaceous deoxygenation must be distinguished from those which

occur in the field. The following terms are used herein to maintain these distinctions:

k_1 = laboratory-derived CBOD decay rate,

k_d = CBOD decay rate in natural waters

k_s = CBOD settling rate

k_R = overall rate of CBOD removal from water column

By these definitions,

$$k_R = k_d + k_s \quad (3-28)$$

$$k_d \geq k_1, \text{ typically} \quad (3-29)$$

Note that uptake/sorption by the benthic biota is not explicitly dealt with. In practice, the effects of instream deoxygenation and benthic biological CBOD removal are difficult to distinguish. Thus reported k_d values may incorporate both processes. Unless otherwise specified, all rate coefficients discussed in this section are corrected to 20°C, are to the base e, and are in units of inverse days.

3.3.4 Factors Affecting CBOD Removal

A number of factors are known to influence the rate at which CBOD is removed from the water column. Chief among these are water temperature, hydraulic factors, stream geometry and the nature of the carbonaceous material. The influence of these factors has been described by both theoretical and empirical formulations.

Like all biochemical processes, CBOD decay occurs at a rate which increases with increasing temperature up to the point where protein denaturation begins. This temperature dependence is generally formulated for a limited range of temperature as:

$$k_T = k_{20} \theta^{(T-20)} \quad (3-30)$$

where k_T = rate constant at temperature T
 k_{20} = rate constant at 20°C
 θ = an empirical coefficient.

This formulation is based on the Arrhenius equation which incorporates the energy of activation of the overall decay reaction. Arrhenius proposed the relationship:

$$\frac{d \ln k}{dT} = - \frac{E}{RT^2} \quad (3-31)$$

where T = absolute temperature, °K
R = universal gas constant
E = activation energy of the reaction
k = rate constant

Integrating Equation (3-31) results in

$$\ln \frac{k}{k_0} = \frac{-E (T-T_0)}{R T_0 T} \quad (3-32)$$

where T_0 = arbitrarily chosen reference temperature, °K
 k_0 = rate constant at temperature T_0

Equation (3-32) can be rewritten as

$$k = k_0 \exp\left(\frac{-E (T-T_0)}{R T_0 T}\right) \quad (3-33)$$

Equations (3-30) and (3-33) are identical if θ is defined as

$$\theta = \exp\left(\frac{-E}{RT_0 T}\right) \quad (3-34)$$

Note that whether $T-T_0$ is in units of °C or °K is of no concern. Thus θ , which is assumed to be independent of temperature in Equation (3-30), really has some slight temperature dependence.

Table 3-13 shows values of θ which have been used for CBOD decay. The value 1.047 is very widely used and corresponds to an energy of activation of 7900 calories per mole measured by Fair et al. (1968). There are limits to the applicability of this approach because the activation energy is not actually constant. Studies by Schroepfer et al. (1964) indicate that the value of 1.047 for θ is valid between 20°C and 30°C, but higher values are appropriate at lower temperatures. Fair et al. (1968) suggest θ values of 1.11 and 1.15 for 10°C and 5°C, respectively. Few water quality models incorporate a varying temperature dependence for CBOD degradation. Some impose temperature limits, generally 5-30°C, outside of which the reaction is considered not to occur. The model SSAM-IV (Grenney and Kraszewski, 1981) adjusts the BOD decay rate for temperature via the expression:

$$k_T = \tau k_{20} \quad (3-35)$$

$$\text{where } \tau = \frac{0.1393 \exp(0.174(T-2))}{0.9 + 0.1 \exp(0.174(T-2))}$$

This is equivalent to varying the value of θ with temperature.

The 1.047 value originated from the work of Phelps and Theriault (Phelps, 1927, Theriault, 1927). The θ value of 1.047 was an average value obtained from three separate studies with a reported standard deviation of 0.005. Moore noted in 1941 that the correlation of the CBOD decay rate with temperature using the Arrhenius model was not strong, since correlation coefficients of 0.56 to 0.78 were obtained (Moore, 1941).

Water turbulence is hypothesized to influence the rate of BOD depletion in a receiving water in several ways. It influences k_s by controlling such processes as scour and sedimentation. Increased turbulence may enhance contact between BOD and the benthic biological community. It also influences the carbonaceous deoxygenation rate, so that laboratory samples which are agitated during incubation yield higher k_1 values than quiescent samples (see Morrissette and Mavinic, 1978, for example). This confounds the use of k_1 values from static laboratory tests in place of field values

TABLE 3-13
VALUES OF THE TEMPERATURE COMPENSATION COEFFICIENT
USED FOR CARBONACEOUS BOD DECAY

θ , Temperature Correction Factor	Temperature Limits ($^{\circ}\text{C}$)	Reference
1.047		Chen(1970) Harleman <u>et al.</u> (1977) Medina (1979) Genet <u>et al.</u> (1974) Bauer <u>et al.</u> (1979) JRB (1983) Bedford <u>et al.</u> (1983) Thomahn and Fitzpatrick (1982) Velz (1984) Roesner <u>et al.</u> (1981)
1.05		Crim and Lovelace (1973) Rich (1973)
1.03-1.06	(0-5)-(30-35)	Smith (1978)
1.075		Imhoff <u>et al.</u> (1981)
1.024		Metropolitan Washington Area Council of Governments (1982)
1.02-1.06		Baca and Arnett (1976) Baca <u>et al.</u> (1973)
1.04		Di Toro and Connolly (1980)
1.05-1.15	5-30	Fair <u>et al.</u> (1968)

of k_d . To more closely duplicate natural conditions, some investigators used stirring during laboratory incubations (NCASI, 1982a). This particular experiment showed no effect of stirring on the reaction kinetics.

Adjustment factors based on stream characteristics have also been used in BOD calculations. Bosko (1966) expressed k_d in terms of k_1 for streams by the expression:

$$k_d = k_1 + n(V/D) \quad (3-36)$$

where V = stream velocity, length/time

D = stream depth, length

n = coefficient of bed activity, dimensionless

The coefficient of bed activity is a step function of stream gradient; values are given in Table 3-14. This expression has been used in a version of QUAL-II applied to rivers in New England (JRB, 1983; Van Benschoten and Walker, 1984; Walker, 1983), by Terry et al. (1984) on the Illinois River, Arkansas, and by Chen and Goh (1981).

TABLE 3-14. COEFFICIENT OF BED ACTIVITY AS A FUNCTION OF STREAM SLOPE
(from BOSKO, 1966)

Stream Slope (ft/mi)	n
2.5	.1
5.0	.15
10.0	.25
25.0	.4
50.0	.6

Stream hydraulic factors may also account for differences between the deoxygenation rate k_d and the overall BOD removal rate k_R . Table 3-15 shows examples of such differences in six U.S. rivers. Higher values of k_R are attributable to settling of particulate BOD. Bhargava (1983) observed rapid settling of particulate BOD just downstream from sewage outfalls in two

Indian rivers, where k_R was several times greater than farther downstream. He modeled this effect by considering the BOD to be composed of two fractions, using the expression:

$$L_t = L_1(1 - \frac{V_s}{D}t) + L_2 \exp(-k_d t) \quad (3-37)$$

where L_t = BOD remaining at downstream travel time t

L_1 = portion of original BOD removed by settling

L_2 = portion of original BOD subject to in-stream degradation

V_s = settling velocity of particulate BOD

D = average stream depth

TABLE 3-15. DEOXYGENATION RATES FOR SELECTED U.S. RIVERS
(ECKENFELDER AND O'CONNOR, 1961)

River	Flow (cfs)	Temp. (°C)	BOD ₅ (mg/l)	k_d^* (day ⁻¹)	k_R^* (day ⁻¹)
Elk	5	12	52	3.0	3.0
Hudson	620	22	13	0.15	1.7
Wabash	2800	25	14	0.3	0.75
Willamette	3800	22	4	0.2	1.0
Clinton	33	--	--	.14-.13	2.5
Tittabawassee	--	--	--	0.05	0.5

*Note: These data are over 20 years old. It is likely that advances in waste treatment have altered the BOD kinetics in these waterways.

Some modelers distinguish between benthic and water-column CBOD removal, and assign rate coefficients to each type. For example, the sum of

settling and benthic biological CBOD uptake is widely portrayed as a first-order process (Baca and Arnett, 1976; Grenney and Kraszewski, 1981; Duke and Masch, 1973; Orlob, 1974):

$$\frac{\partial L}{\partial t} = -(k_d + k_3)L \quad (3-38)$$

where k_d = water-column deoxygenation rate

k_3 = total removal rate to the benthos by settling and sorption

The settling rate alone may be derived from the particle settling velocity and mean depth of the water column:

$$k_s = \frac{V_s}{D} \quad (3-39)$$

The effects of scour are often incorporated into the benthic removal coefficient k_3 . This may be done implicitly, or by calculating k_3 as the sum of two first-order coefficients having opposite sign (Bauer et al., 1979). Scour of benthic BOD is also treated as a zero-order process (e.g., Baca et al., 1973):

$$\frac{\partial L}{\partial t} = -k_R L + L_a \quad (3-40)$$

where L_a = rate of BOD re-entrainment by scour, mg/(l-day).

The nature of the oxygen-demanding material also affects the rate of its removal from a receiving water. Particulate BOD, while it may be susceptible to settling, is more refractory than soluble BOD. Also two waters having the same ultimate BOD may show very different BOD depletion profiles. For in-stream BOD arising from a wastewater inflow, the degree of treatment of the wastewater is important. In general, the higher the degree of treatment, the greater the degree of waste stabilization, and the lower the deoxygenation rate will be. Fair et al. (1968) cite deoxygenation rates of 0.39, 0.35 and 0.12-0.23 per day for raw wastewater, primary and secondary effluent, respectively.

Martone (1976) observed a similar trend with paper industry wastewaters. Following biological treatment, rates as low as 0.02 per day, base e were observed. This low rate was attributed to the refractory humic material remaining in the wastewater. Similar low rates were also noted in receiving streams (NCASI, 1982a).

The U.S. Environmental Protection Agency (1983), using the data of Hydrosience (1971) and Wright-McDonnell (1979) has derived a relationship between stream depth and CBOD removal. This is shown in Figure 3-11. Note that the predicted decay rate corresponds to the sum of water column and benthic deoxygenation. Should SOD data be available, modelers are cautioned when using this figure to avoid double counting of SOD in the oxygen balance.

To this point, depletion of dissolved oxygen caused by CBOD decay has been implicitly considered to depend only on the concentration of substrate, i.e., CBOD. However, at low dissolved oxygen concentrations, oxygen may be limiting to the reaction. Provision for this "oxygen inhibition" is incorporated into many water quality models as discussed below.

Autochthonous sources may be a major influence on BOD dynamics. In lakes, carbon fixed by phytoplankton may become the predominant source of CBOD. Investigators have dealt with the input of autochthonous CBOD in several ways. Modeling Onondaga Lake in New York, Freedman et al. (1980) considered the biological contribution to water-column CBOD to be equivalent to the mass rate of phytoplankton production of organic material. Baca and Arnett (1976) considered the death rates of phytoplankton and zooplankton separately. These affected BOD according to the expression:

$$\frac{\partial L}{\partial t} = -k_d L + \alpha (F_p P + F_z Z) \quad (3-41)$$

where α = stoichiometric coefficient, mgO_2/mgC

F_z = death rate of zooplankton from fish predation, 1/day

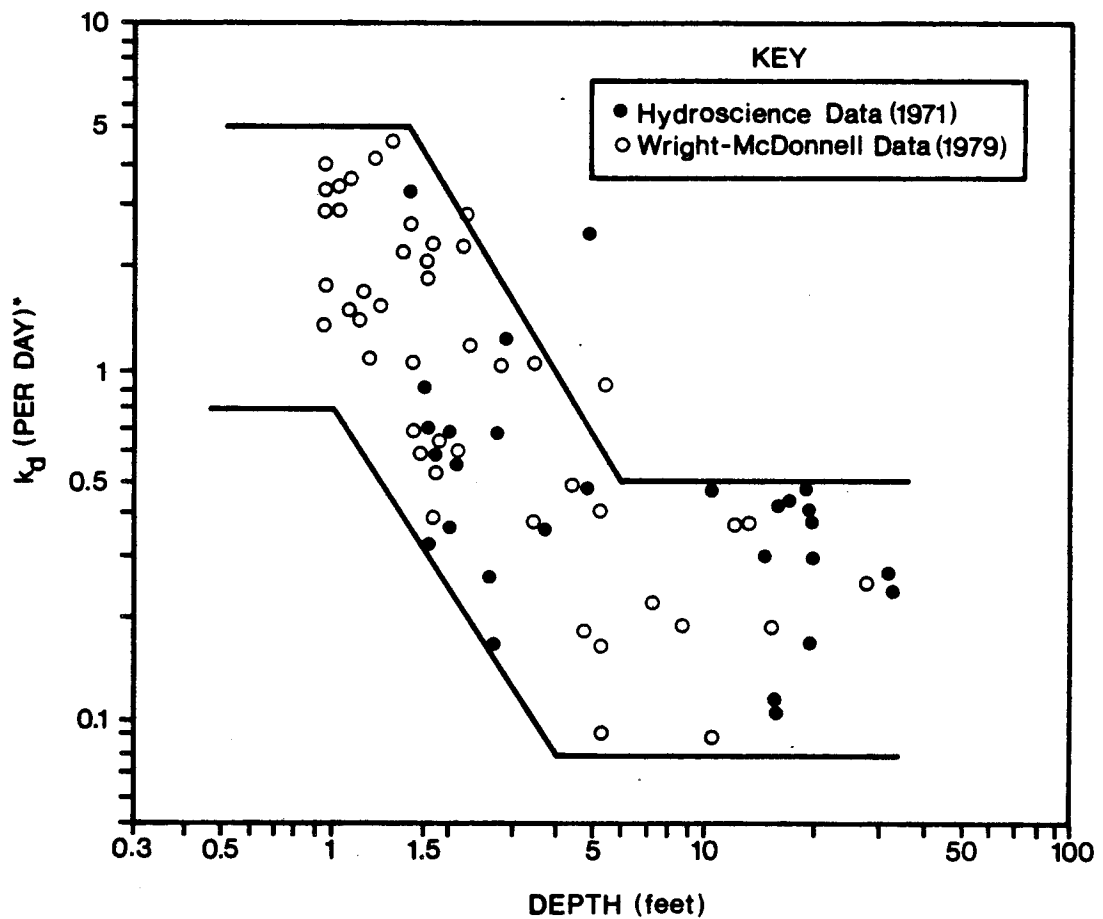
F_p = death rate of phytoplankton from zooplankton grazing, 1/day

P = phytoplankton concentration, mg-C/l

Z = zooplankton concentration, mg-C/l

A Potomac Estuary Model by Thomann and Fitzpatrick (1982) considers the "non-predatory" death rate of phytoplankton to augment water-column CBOD:

$$\frac{\partial L}{\partial t} = -k_d L + \alpha k_{1D} P_c / BOD_{u5} \quad (3-42)$$



*NOTE: k_d includes a
Benthic Deoxygenation
Component

Figure 3-11. Deoxygenation coefficient (k_d) as a function of depth

where k_{1D} = death rate of phytoplankton other than from grazing,
1/days

P_c = phytoplankton carbon, mg/l

BOD_{u5} = ratio of ultimate to 5-day CBOD, taken as 1.85 for
phytoplankton

3.3.5 Predictive Expressions for Deoxygenation

The carbonaceous deoxygenation rate is determined in two general ways. Most investigators base their measures of k_d on the results of field or laboratory experiments that monitor dissolved oxygen or ultimate CBOD. In stream modeling, this traditional approach has recently been augmented by efforts to quantify k_d as a function of hydraulic parameters.

It is important to note that these correlations relied upon published values of k_d (such as Figure 3-11). No distinction was made as to how k_d was obtained; and in these correlations, observed instream values have equal weight with measured laboratory values. Thus, considerable ambiguity exists in the published literature with regard to the meaning of k_d and the resulting correlation may be of limited value.

Bansal (1975) attempted to predict deoxygenation rates based on the Reynolds number and the Froude number. This approach was found to have limited applicability (Novotny and Krenkel, 1975). More commonly, k_d is found as a function of flow rate, hydraulic radius or average stream depth. Wright and McDonnell (1979) utilized data from 36 stream reaches in the U.S. to derive the expression:

$$k_d = (10.3)Q^{-0.49} \quad (3-43)$$

where Q = flow rate, ft^3/sec

They found that above flow rates of about $800 \text{ ft}^3/\text{sec}$, k_d is not a function of flow rate. The lower limit of the applicability of this expression is approximately $10 \text{ ft}^3/\text{sec}$. Below this flow rate, deoxygenation

rates were noted to consistently fall in the range 2.5-3.5 per day, independent of streamflow. For this same range of flowrates (between 10 and 800 cfs), an expression based on channel wetted perimeter was also found successful in predicting k_d :

$$k_d = 39.6P^{-0.84} \quad (3-44)$$

where P = wetted perimeter, feet

The deoxygenation rate coefficient has also been expressed as an exponential function of stream depth (Hydroscience, 1971; Medina, 1979) and hydraulic radius (Grenney and Kraszewski, 1981).

Regardless of how carbonaceous deoxygenation rate coefficients are derived, they are widely applied in only two ways: first-order decay and simultaneous first-order decay. In the latter case, the CBOD is partitioned into more than one fraction; each fraction is degraded at a specific rate according to first-order kinetics. The first-order approximation for CBOD decay has been widely criticized, and multi-order or logarithmic models have been used by individual investigators (see Hunter, 1977 for a review).

Martone (1976), in a study of BOD kinetic models, observed that first order kinetics did not universally describe observed BOD data. In a few cases, a two-stage carbonaceous BOD model resulted in a better statistical fit (McKeown et al., 1981). The Wisconsin Department of Natural Resources included this alternative formulation in its QUAL-III model (Wisconsin DNR, 1979). However, no alternative formulation has been shown to be universally superior, and oxygen-sag computations are comparatively easily performed for first-order decay. Hence, this is the pre-eminent model in use today.

Table 3-16 shows the expressions used by water quality modelers to describe the consumption of oxygen as a function of water column CBOD decay. Note that nonoxidative processes such as settling, where CBOD is removed from or added to the water column, do not contribute to dissolved oxygen

TABLE 3-16. EXPRESSIONS FOR CARBONACEOUS OXYGEN DEMAND
USED IN WATER QUALITY MODELS

Depletion Rate of Dissolved Oxygen by CBOD Decay, $\frac{\partial DO}{\partial t}$	Model and Reference
$-k_d L$	MIT-DNM (Harleman <i>et al.</i> , 1977) Dynamic Estuary Model (DEM) (Genet <i>et al.</i> , 1974) EXPLORE-I (Baca <i>et al.</i> , 1973) USGS river model (Bauer <i>et al.</i> , 1979) HSPF (Inhoff <i>et al.</i> , 1981) DOSAG3 (Duke and Masch, 1973) DIURNAL (Deb and Bowers, 1983) QUAL-II (Roesner <i>et al.</i> , 1981) O'Connor <i>et al.</i> (1981)*
$-k_d L \frac{O_2}{k_{O_2} + O_2}$	Lake Erie Model* (Di Toro and Connolly, 1980) Potomac Estuary Model (PEM) (Thomann and Fitzpatrick, 1982)
$-aD^b L$	Level III-Receiving (Medina, 1979)
$-aQ^b L$	Wright and McDonnell (1979) Rinaldi (1979)
$-aQ^b L \frac{O_2}{k_{O_2} + O_2}$	Bedford <i>et al.</i> (1983)
$-k_1 L_{sol} - k_2 L_{det}$	WRRS (Smith, 1978) CE-QUAL-R1* (Corps of Engineers, 1982) Chen <i>et al.</i> * (1974)
$-k_d L \left(\text{depth, } D > 2.44m \right) \left\{ \begin{array}{l} -0.434 \\ \left(\frac{D}{2.44} \right) k_d L \text{ (} D < 2.44m \text{)} \end{array} \right\}$	RECEIV-II (Raytheon, 1974) WRECEV (Johnson and Duke, 1976)
$-C_1 (R_h C_2)_L$	SSAM-IV (Grenney and Kraszewski, 1981)
$-k_d \phi_c L$	Freedman <i>et al.</i> (1980)

*"L" represents a fraction of organic carbon, soluble and/or detrital, rather than CBOD.

Definition of symbols:

k_d	field CBOD oxidation rate
L	carbonaceous BOD concentration
O_2	concentration of dissolved oxygen
k_{O_2}	half-saturation constant for oxygen
a, b, C_1, C_2	empirically-determined coefficients
D	water depth
Q	stream flow rate
k_1, k_2	oxidation rates for two CBOD fractions
L_{sol}	soluble CBOD (or, dissolved organic carbon)
L_{det}	particulate CBOD (particulate organic carbon)
R_h	stream hydraulic radius
ϕ_c	nonlinear O_2 inhibition coefficient

depletion, and are not included in the expressions. In cases where k_d is calculated within the model using a hydraulic expression, that expression is included in the table. As shown, the rate expressions do not include temperature correction coefficients. Some of the models listed (starred references) do not treat CBOD per se, but organic carbon or carbonaceous detritus. The effect of low dissolved oxygen concentration is generally handled through a Michaelis-Menten formulation. A representative value of k_{O_2} , the half-saturation coefficient for oxygen uptake, is 0.5 mg/l. Some models partition oxygen-demanding matter into soluble and particulate fractions, with different rate coefficients. In limnological models, the particulate or detrital fraction may be determined as a function of the death of phytoplankton and zooplankton, with no additional particulate CBOD present.

3.3.6 Values of Kinetic Coefficients

Table 3-17 is a compilation of deoxygenation rate coefficients and the methods by which they were determined. Unless otherwise specified, the coefficient is k_d . In some cases, investigators reported k_R values as such; in other cases, rates reported as deoxygenation were actually observations of total removal (k_R) and they are cited as such. Most of the data are from rivers, although some lake and estuary values have been reported. The range of values reported as in-stream deoxygenation rates is wide, spanning more than two orders of magnitude.

3.3.7 Measurement of Ultimate BOD Decay Rate

In laboratory studies using BOD bottles, BOD exertion is found as the difference between sample and control dissolved oxygen depletion. Respirometry studies and reaerated stirred-reactor studies involve essentially continuous monitoring of oxygen usage. The results of these laboratory experiments produce cumulative oxygen demand-vs-time relationships.

A number of methods have been used to derive k_1 from these curves. Among these are:

TABLE 3-17. VALUES OF KINETIC COEFFICIENTS FOR DECAY
OF CARBONACEOUS BOD

Location	k_d (1/days @ 20°C, base e)	Method of Determining Coefficient	Reference
Potomac Estuary 1977 1978	0.14 ± 0.023 0.16 ± 0.05	field study	US EPA (1979a) US EPA (1979b)
Willamette River, OR	0.1-0.3		Baca <u>et al.</u> (1973)
Chattahoochee River, GA	0.16		Bauer <u>et al.</u> (1979)
Ganga River, India Yamuna River, India	3.5-5.6 (k_R) 1.4	field study	Bhargava (1983)
S. Fork, Shenandoah River	0.4(k_R)	field study	Deb and Bowers (1983)
Merrimack River, Mass	0.01-0.1	field study	Camp (1965)
Gray's Creek, Louisiana	1.44 (k_R)	model calibration	Crane and Malone (1982)
Onondaga Lake, New York	0.10	model calibration	Freedman <u>et al.</u> (1980)
Yampa River, Colorado	0.40	model calibration	Grenney and Kraszewski (1981)
Skravad River, Denmark	0.15 0.90 (k_R)	field study	Hvitved-Jacobsen (1982)
Seneca Creek	0.008		Metropolitan Washington Council of Governments (1982)
Kansas (6 rivers) Michigan (3 rivers) Truckee River, Nevada Virginia (3 rivers) N. Branch, Potomac, WV South Carolina (3 rivers) New York (2 rivers) New Jersey (3 rivers) Houston Ship Channel, TX Cape Fear R. Estuary, NC	0.02-0.60 0.56-3.37 0.36-0.96 0.30-1.25 0.4 0.3-0.35 0.125-0.4 0.2-0.23 0.25 0.23	various methods	Reported by Bansal (1975)
Holston River, Tenn	0.4-1.5	model calibration	Novotny and Krenkel (1975)
New York Bight	0.05-0.25		O'Connor <u>et al.</u> (1981)
White River, Arkansas	0.004-0.66 (k_1)	laboratory study	Terry <u>et al.</u> (1983)
N. Fork Kings River, CA	0.2		Tetra Tech (1976)
Lake Washington, WA	0.2		Chen and Orlob (1975)
Ouachita River, Arkansas	0.15 0.17 (k_R) 0.02 (k_1)	calibration laboratory study	Hydroscience (1979) NCASI (1982a)
36 U.S. river reaches plus laboratory flume	0.08-4.24	field studies	Wright and McDonnell (1979)
San Francisco Bay Estuary	0.2		Chen (1970)
Boise River, ID	0.75		Chen and Wells (1975)
W. Fork, Trinity River, TX	0.06-0.30	laboratory study	Jennings <u>et al.</u> (1982)

TABLE 3-17. (Cont'd)

Location	k_d (1/days @ 20°C, base e)	Method of Determining Coefficient	Reference
Willamette River, OR	0.07-0.14	lab and field field study	McCutcheon (1983)
Arkansas River, CO	1.5		
Lower Sacramento River, CA	0.41		Hydroscience (1972)
Delaware River Estuary	0.31		
Wappinger Creek Estuary, NY	0.31		
Potomac Estuary	0.16, 0.21		Thomann and Fitzpatrick (1982)
Speed River, Ontario	1.0	field study	Gowda (1983)

1. The linear least-squares technique of Reed and Theriault
2. Thomas' graphical slope method
3. The moment method of Moore (1941)
4. Orford and Ingram's logarithmic method
5. Rhame's two-point method
6. Nemerow's general laboratory method (graphical)
7. The daily difference method of Tsivoglou (1958)
8. The rapid ratio method of Sheehy (1960)
9. Nonlinear regression method of NCASI (1982d).

The first six methods are discussed by Nemerow (1974). Gaudy *et al.* (1967) review and compare a number of calculation methods. Some of the techniques assume a particular kinetic model for the data, while others do not. The linear least-squares method can be used with a first or second-order BOD dependency, with somewhat different calculations. Orford and Ingram's method assumes that cumulative BOD exertion varies with the logarithm of elapsed time, and no limiting value is approached. The nonlinear regression technique has the advantage of flexibility in evaluating alternative BOD models.

Barnwell (1980) developed a nonlinear least-squares technique for fitting laboratory CBOD progressions. It is based upon the first-order decay model, and is suitable for implementation on programmable calculators or microcomputers. It allows computation of confidence contours for the estimates of k_1 and ultimate CBOD. The nonlinear regression technique also

provides estimates of the confidence contours. Further discussion of BOD measurement techniques are contained in Stover and McCartney (1984) and Stamer et al. (1983).

Estimates of the length of time necessary to evaluate the BOD parameters have been provided by Berthouex and Hunter (1971). They determined, using statistical arguments, that this length of time is a function of the anticipated decay rate, k_1 . The time computed from $4/k_1$ is suggested as the maximum value. Barnwell (1980) and NCASI (1982d) have shown that the estimate of the confidence contours is directly related to the length of time the BOD experiment was conducted. As the length of time increases, the confidence contours get smaller.

In field estimation of deoxygenation rates, water samples from along the stream reach are collected, and their ultimate CBOD values are determined in the laboratory. Graphical methods are then used to find the CBOD decay rate. These techniques are based on a mass balance for BOD in the stream. Note that if unfiltered water samples are used, the rate calculated is k_R , not k_d . It may be that the two rates are essentially equivalent. An unvarying profile of suspended solids along the reach may indicate the validity of these measurements to estimate k_d . Alternatively, filtered samples may be incubated, and the contribution of particulate matter to BOD assumed to be insignificant.

The calculation methods described herein are based upon simplified forms of the BOD mass-balance equations. The user should assess carefully whether the necessary simplifying assumptions can reasonably be applied to the study system.

One simple and commonly used technique is for streams influenced by continuous point sources. The stream reach under study should have a relatively constant cross section, constant flow rate, and a single point-source BOD loading. The BOD concentration downstream from the source is given by:

$$L = L_0 \exp \left(\frac{-k_R X}{V} \right) \quad (3-45)$$

where X = distance downstream from source, length

L_0 = BOD concentration immediately downstream from source, at
 $X = 0$, mass/volume

V = average stream velocity, length/time

A graph of the logarithm of BOD concentration versus distance downstream should show a straight-line relationship with a slope of $-k_R/V$ if decay is first order. Sometimes the slope may be more steep for the first few miles below a point source, where settling of BOD as well as decay is occurring (Deb and Bower, 1983). The slope may be found graphically or by linear regression. Figure 3-12 is an example of this type of computation. If the slope is determined by regression, the natural log of BOD should be regressed on distance. If the slope is found graphically from a semi-log plot, it must be multiplied by 2.3 (to convert from base-10 to base-e) for model applications.

The same approach is possible for tidally influenced rivers, as discussed in Zison et al. (1978). However, the tidally averaged dispersion coefficient is required as an additional piece of information and will add some degree of uncertainty to the predicted k_d value.

3.3.8 Summary and Recommendations

Although its shortcomings have been widely discussed, the first-order model is still the common method for simulating instream CBOD kinetics. Relative ease of computation, a long history of use and the absence of alternative formulations which are superior over a range of conditions are probably responsible for this precedent.

In estimating k_d , there is increasing use of various stream hydraulic parameters. Estimates based on flow rate seem to be most successful,

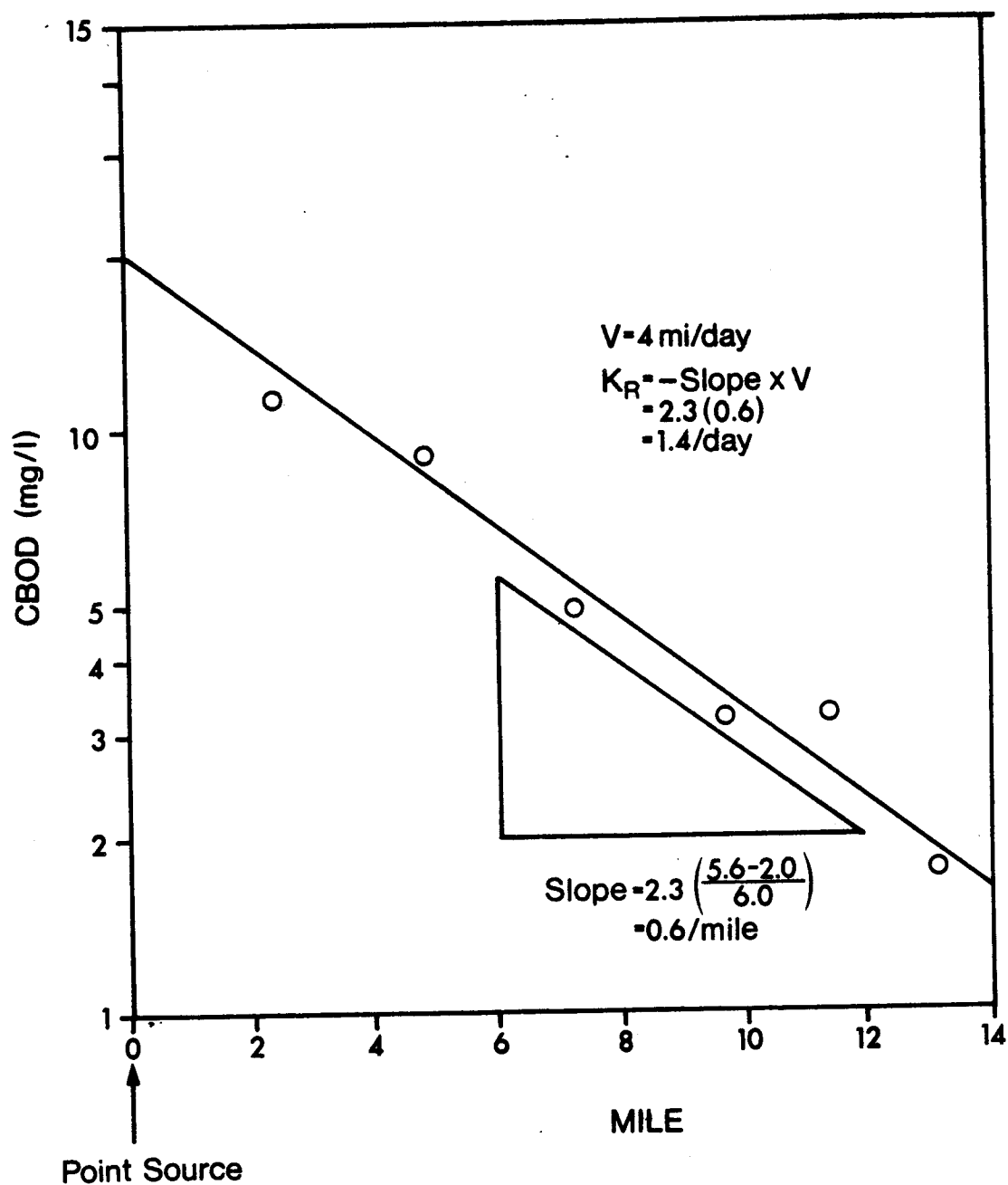


Figure 3-12. Example computation of k_R based on BOD measurements of stream water.

although stream geometric parameters such as hydraulic radius and depth are also used. The use of hydraulic characteristics for k_d prediction has limits, since deoxygenation is independent of flow rate at both high and low flow. These predictive equations should be used with caution.

To assess CBOD fluxes based on site-specific data, it is essential to have some familiarity with the water body under study. A reconnaissance survey can help elucidate the possible importance of CBOD sedimentation or resuspension, as well as the magnitude of aquatic biological processes. The survey is also an opportunity to assess what assumptions can reasonably be made about the system to simplify calculations.

For those river waters and effluents which contain significant concentrations of NBOD, the analyst must consider an appropriate procedure for the separation of NBOD from CBOD in the ultimate BOD test. Currently, two techniques are used which include: the use of nitrification inhibitors such as TCMP and others, and the monitoring of nitrogen series with time during the test to define the NBOD. There is currently no consensus as to which technique is best. Nitrification inhibitors have been observed to have an unpredictable inhibition effect on the CBOD kinetics as well (Martone, 1976). For large modeling projects, the monitoring of nitrogen species in the BOD bottle tests can create significant additional laboratory expense. Though likely to be more expensive, the latter technique provides more information regarding the CBOD and NBOD kinetics and is recommended by NCASI (1982b).

The investigator should exercise caution in using deoxygenation coefficients obtained for other water bodies. The wide range of values in Table 3-17 indicates substantial variation in rate estimation and reporting procedures. Unfortunately, many investigators automatically equate k_1 or k_R with k_d , and do not fully consider the different meanings of these rates. Some report k_d and k_R values without stating whether these apply to total BOD or CBOD, are temperature-corrected, are to base e or base 10, etc.

One way to handle these uncertainties is to conduct sensitivity analyses of model predictions. Such analyses are beyond the scope of many projects; however, results are available for many widely-used models either in the model documentation or in the final reports of large-scale projects. Examples of sensitivity analyses for deoxygenation rate coefficients are Crane and Malone (1982), Thomann and Fitzpatrick (1982) and NCASI (1982a).

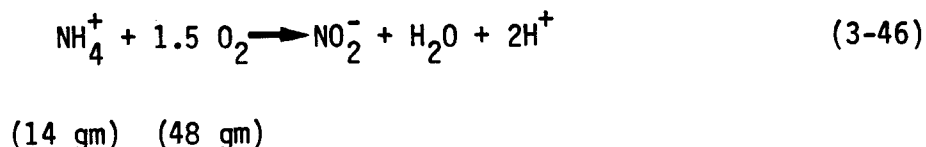
In addition, it is possible to quantitatively evaluate the uncertainty associated with an estimated coefficient. Barnwell's (1980) and NCASI's (1982b) calculation techniques allow computation of confidence limits for an estimated k_1 value. Jaffe and Parker (1984) provide a procedure for estimating the uncertainty of k_d values as influenced by the field sampling scheme. Chadderton *et al.* (1982) evaluate the relative contributions to uncertainty of the parameters of the Streeter-Phelps equation.

3.4 NITROGENOUS BIOCHEMICAL OXYGEN DEMAND

3.4.1 Introduction

The transformation of reduced forms of nitrogen to more oxidized forms (nitrification) consumes oxygen. Although nitrification is also a nutrient transformation process, this section addresses the oxygen consumption aspects, since numerous models simulate nitrogenous biochemical oxygen demand (NBOD) without detailing nitrogen transformations.

Nitrification is a two-stage process. The first stage is the oxidation of ammonia to nitrite by Nitrosomonas bacteria:

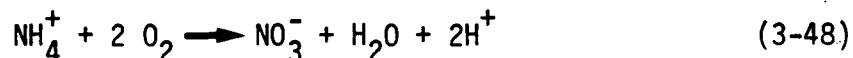


Stoichiometrically 48/14 or 3.43 gm of oxygen are consumed for each gram of ammonia-nitrogen oxidized to nitrite-nitrogen. During the second stage of nitrification Nitrobacter bacteria oxidize nitrite to nitrate:



(14 gm) (16 gm)

Stoichiometrically $16/14 = 1.14$ gm of oxygen are consumed per gram of nitrite-nitrogen oxidized. If the two reactions are combined, the complete oxidation of ammonia can be represented by:



(14 gm) (64 gm)

As expected, $64/14 = 4.57$ gm of oxygen are required for the complete oxidation of one gram of ammonia.

In the reactions above, the organic-nitrogen form does not appear, since organic-nitrogen is hydrolyzed to ammonia, and does not consume oxygen in the process. However, organic nitrogen will eventually contribute to the NBOD, as the following equation shows:

$$\text{NBOD} = 4.57 (\text{N}_0 + \text{N}_1) + 1.14 \text{N}_2 \quad (3-49)$$

where N_0 = organic-nitrogen concentration, mass/volume

N_1 = ammonia-nitrogen concentration, mass/volume

N_2 = nitrite-nitrogen concentration, mass/volume

The stoichiometric coefficients of 3.43, 1.14, and 4.57 in the equations above are actually somewhat higher than the total oxygen requirements because of cell synthesis. Some researchers (e.g., Wezernak and Gannon, 1967 and Adams and Eckenfelder, 1977) have suggested that the three coefficients be reduced to 3.22, 1.11, and 4.33, respectively.

3.4.2 Modeling Approaches

Modelers use both the two-stage and one-stage approach to simulate NBOD decay, as shown by Table 3-18. First order kinetics is the predominant

method used to simulate the process. Oxygen limitation is used by some modelers (e.g., O'Connor et al., 1981; Thomann and Fitzpatrick, 1982; and Bedford et al., 1983).

Relatively few modelers explicitly simulate the effects of benthic nitrification (exceptions are Williams and Lewis, 1984 and Mills, 1976). The models of Williams and Lewis, and Mills were developed for relatively shallow streams where bottom effects could be important. Of these two, only Mills looks at the details of oxygen and nitrogen transfer from the water column into an attached nitrifying biofilm. Several studies (Kreutzberger and Francisco, 1977; Koltz, 1982) have confirmed that nitrifying bacteria can thrive in the beds of shallow streams, and that, in the streams they investigated, nitrification occurred primarily in the bed, and not in the water column. Denitrification has been shown to occur in stream sediments

TABLE 3-18. EXPRESSIONS FOR NITROGENOUS BIOCHEMICAL OXIDATION RATES USED IN A VARIETY OF WATER QUALITY MODELS

Expression for Nitrogenous Oxidation	Model and/or Reference
Rate, $\partial DO/\partial t$	
$-a_1 k_{n1} N_1 - a_2 k_{n2} N_2$	WQRRS (Smith, 1978) Bauer <u>et al.</u> (1979) QUAL-II (Roesner <u>et al.</u> , 1981) SSAM IV (Grenney and Kraszewski, 1981) CE-QUAL-R1 (U.S. Army COE, 1982) RECEIV II (Raytheon, 1974) NCASI (1982d) Baca and Arnett (1976) MIT Transient Water Quality Model (Harleman <u>et al.</u> , 1977) DOSAG3 (Duke and Masch, 1973) HSPF (Imhoff <u>et al.</u> , 1981) Genet <u>et al.</u> (1974)
$-k_n L_n$	DIURNAL (Deb and Bowers, 1983) Gowda (1983) EXPLORE-1 (Baca <u>et al.</u> , 1973) Bauer <u>et al.</u> (1979) Di Toro and Matystik, 1980

TABLE 3-18. (Cont'd)

Expression for Nitrogenous Oxidation Rate, $\partial DO/\partial t$	Model and/or Reference
$-a_3 k_n \frac{O_2}{O_2 + K_{nit}} N_1$	O'Connor <i>et al.</i> (1981) Thomann and Fitzpatrick (1982)
$-a_3 a_4 Q^b \frac{O_2}{O_2 + K_{nit}} N_1$	Bedford <i>et al.</i> (1983)
Time Shifted First Order (time delayed)	NCASI (1982d)
Lagged First Order (nonoxidative step followed by an oxidative step)	NCASI (1982d)
Benthic Nitrification:	
$-a_3 S_n$ (zero order kinetics)	Williams and Lewis (1984) Bauer <i>et al.</i> (1979)
$-J_c$ (Monod kinetics)	Mills (1976)

Definition of Symbols:

k_{n1} = ammonia to nitrite oxidation rate
 k_{n2} = nitrite to nitrate oxidation rate
 k_n = NBOD decay rate
 a_1 = 3.43, typically
 a_2 = 1.14, typically
 a_3 = 4.57, typically
 a_4, b = unspecified
 N_1 = NH_4^+ -N
 N_2 = NO_2^- -N
 L_n = nitrogenous BOD

O_2 = dissolved oxygen concentration
 K_{NIT} = half-saturation constant
 S_n = zero order benthic nitrification rate
 J_c = benthic oxygen flux rate by nitrifying
 organisms growing in an attached
 biofilm

as well (Wyer and Hill, 1984). Denitrification is discussed in more detail in Chapter 5.

The most straightforward method of including the effects of organic nitrogen on the potential depletion of dissolved oxygen is to simulate the conversion of organic nitrogen to ammonium nitrogen (a rate of 0.1/day is typically used). The increased ammonia concentration is then available to exert an oxygen demand. However, it is not clear that all the models in

Table 3-18 simulate the organic nitrogen to ammonia conversion. Some models appear to combine ammonia and organic nitrogen together into a single term.

While first order kinetics is the most popular approach for simulating nitrification in natural systems, Monod and zero-order kinetics are often used to simulate nitrification in wastewater treatment processes (Hall and Murphy, 1980; Charley et al., 1980; Rittmann and McCarty, 1978). Figure 3-13 shows how nitrification is simulated using Monod kinetics. At the high level of reduced nitrogen compounds found in wastewater, nitrification can proceed at its maximum rate, and thus is zero order (independent of substrate concentration). At lower reduced nitrogen concentrations, first order kinetics are applicable.

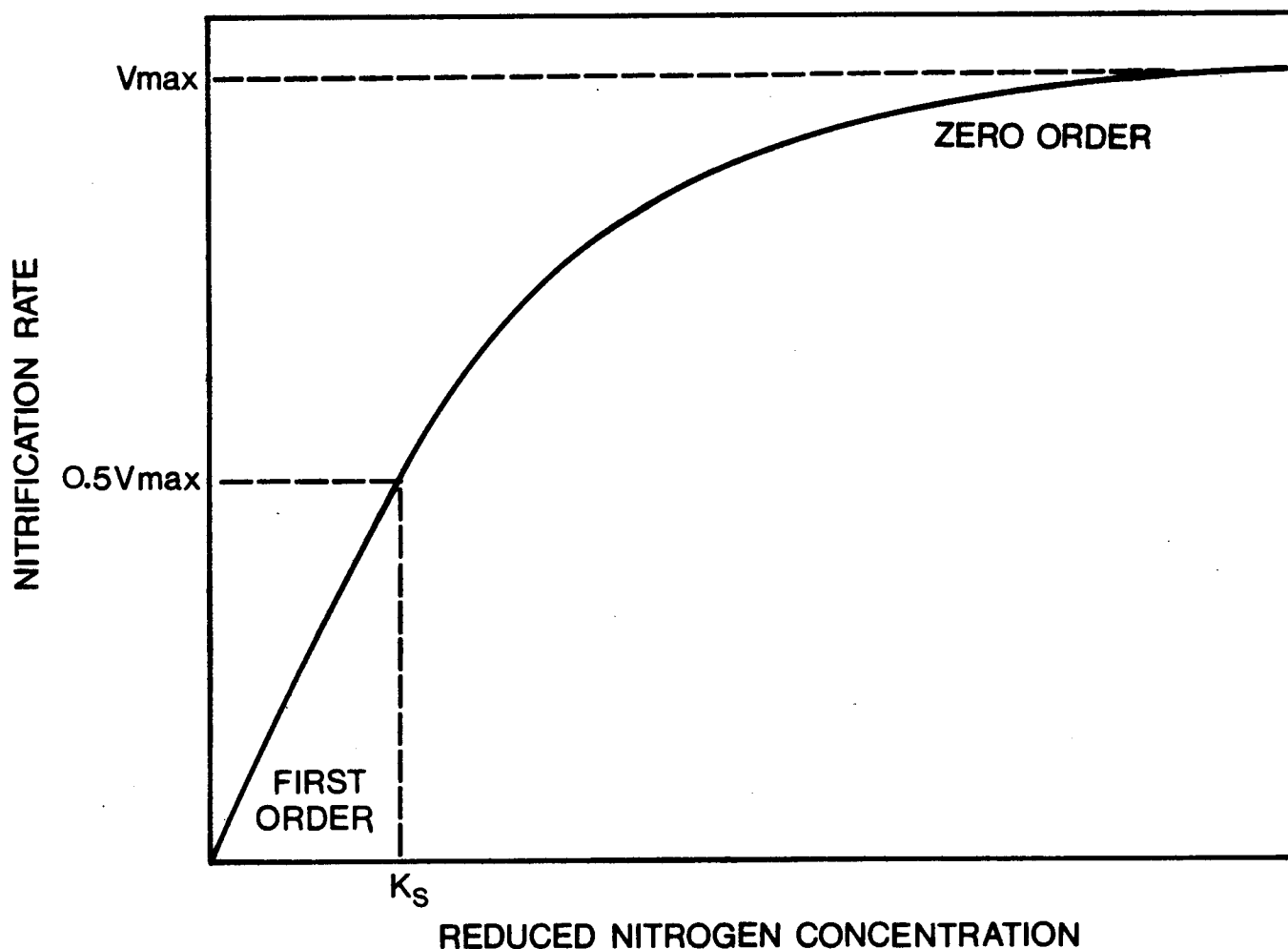


Figure 3-13. Effect of Reduced Nitrogen Concentration on Nitrification Rate as Reported by Borchardt (1966).

Several researchers (e.g., Wild et al., 1971; Kiff, 1972; Huang and Hopson, 1974) have established concentration ranges of ammonia nitrogen when zero order kinetics appear to be followed. The range is quite wide, from 1.6 mg/l to 673 mg/l. Concentrations of ammonia-nitrogen in natural waters can exceed the lower end of the scale reported, and indicate that zero order or Monod kinetics may be appropriate in these circumstances (e.g., see Wilber et al., 1979).

3.4.3 Factors That Affect Nitrification

Table 3-19 summarizes studies that have investigated factors that influence the rate of nitrification. The factors include pH, temperature, ammonia and nitrite concentrations, dissolved oxygen, suspended solids, and organic and inorganic compounds. Sharma and Ahlert (1977) also provide a review of previous studies.

Many of the studies have been carried out in controlled environments, and not in natural waters. Also, the concentration of organic substances which have inhibitory effects on nitrification are often, but not always, well above 1 mg/l (Wood et al., (1981)), so that the compounds are not likely to be inhibitory in natural waters.

Modelers typically consider only the temperature effect on nitrification, although a few do model dissolved oxygen limitations (see Table 3-18). Other inhibitory or stimulatory effects are assumed to be included in the "reference" rate (typically at 20°C) measured or otherwise selected for the modeling applications.

Researchers have found that within the temperature range of 10°C to 30°C temperature effects can be simulated by the following expression:

$$k_n = k_{n20} \theta^{T-20} \quad (3-50)$$

where k_{n20} = nitrification rate coefficient at 20°C
 θ = temperature correction factor

TABLE 3-19. SUMMARY OF FACTORS THAT INFLUENCE NITRIFICATION

Reference	Factors Investigated	Comments
Sharma and Ahlert (1977)	Temperature, pH, Nitrogen Concentrations, Dissolved Oxygen, Organic Compounds	In reviews of previous studies found: 12 studies for dissolved oxygen, 15 studies for pH, 14 studies for the effect of ammonia levels on nitrification, 11 studies of effects of nitrate levels on nitrification, 34 studies on substances that are required or stimulate nitrification; 47 studies on substances that inhibit nitrification.
Stenstrom and Poduska (1980)	Dissolved Oxygen	In this literature review of the effects of dissolved oxygen concentrations on nitrification, the lowest concentration where nitrification occurred is approximately 0.3 mg/l. However, the dissolved oxygen level required for no oxygen inhibition varied to as high as 4.0 mg/l, while other researchers found only 0.5 mg/l is required.
Wild, Sawyer, and McMahon (1971)	pH, Temperature, Ammonia-nitrogen	Studies were conducted in a pilot nitrification unit receiving trickling filter effluent. Ammonia nitrogen did not inhibit nitrification at concentrations less than 60 mg/l. Optimum pH for nitrification was found to be 8.4. The rate of nitrification increased with temperature in the range 5°C to 30°C.
Kholdebarin and Oertli (1977a)	pH, Ammonia-nitrogen	For water samples collected from the Whitewater River, California, the optimum pH for nitrification of ammonia and nitrite was 8.5. Nitrite oxidation was stimulated by the addition of 3 mg/l ammonium.
Kholdebarin and Oertli (1977b)	Suspended Solids	In water from the Whitewater River in California, suspended solids were found to have a stimulatory effect on nitrification, presumably caused by the physical support provided by the solids.
Bridle, Climenhage, Stelzig (1979)	pH, Temperature, Ammonia-nitrogen, Copper	In batch reactors ammonia nitrification was not inhibited for TKN levels up to 340 mg/l. The optimum pH for nitrification was 8.5. The nitrification rate increased approximately 2.5 fold for each 10°C increase. Copper concentrations of 3000 mg/l produced no adverse effect; concentrations of 6000 mg/l were inhibitory.
Quinlan (1980)	Temperature	Temperature for optimal ammonia and nitrite oxidation was found to depend on nitrogen concentrations. At low nitrogen concentrations the optimum temperatures were 35.4°C for ammonia oxidation and 15.4°C for nitrite oxidation.
Wood, Hurley, Matthews (1981)	Organic Compounds	Laboratory studies were conducted using filtered liquor from return activated sludge. Approximately 20 compounds were tested in concentrations from 10 to 330 mg/l. Approximately half the compounds had no inhibitory effects.
Hockenbury and Grady (1977)	Organic Compounds	This study reviewed previous work on the influence of organic compounds on nitrification. Additionally, they found that many compounds did not inhibit nitrification at concentrations as high as 100 mg/l, while other compounds inhibited nitrification at concentrations less than 1 mg/l.

Values of the temperature correction factor are reported in Table 3-20. Temperature correction values are slightly higher for ammonia oxidation than for nitrite oxidation. The mean temperature correction values are 1.0850 for ammonia oxidation and 1.0586 for nitrite oxidation. Many models use temperature correction factors slightly lower than these values. Typically modelers use only one temperature correction coefficient, and do not distinguish between temperature corrections for ammonia and nitrite oxidation. Example of temperature correction factors used in selected models are:

- 1.05, EXPLORE-1 (Baca et al., 1973)
- 1.065, MIT Nitrogen model (Harleman et al., 1977)
- 1.08, New York Bight model (O'Connor et al., 1981)
- 1.047, QUAL-II (Roesner et al., 1981), USGS Steady State Model (Bauer et al., 1979)
- 1.045, Potomac Estuary Model (Thomann and Fitzpatrick, 1982)

TABLE 3-20
TEMPERATURE CORRECTION FACTOR, θ , FOR NITRIFICATION

Reference	Ammonia Oxidation	Nitrite Oxidation
Stratton (1966); Stratton and McCarty (1967)	1.0876	1.0576
Knowles <u>et al.</u> (1965)	1.0997	1.0608
Buswell <u>et al.</u> (1957)	1.0757	-
Wild <u>et al.</u> (1971)	1.0548	-
Bridle <u>et al.</u> (1979)	1.1030	-
Sharma and Ahlert (1977)	1.069	1.0470
Laudelout and Van Tichelen (1960)	-	1.0689
<u>Mean</u>	<u>1.0850</u>	<u>1.0586</u>

- 1.02-1.03, WQRRS (Smith, 1978)
- 1.08, Lake Erie model (Di Toro and Connolly, 1980)

While Equation (3-44) can provide adequate temperature correction up to approximately 30°C, beyond this temperature the nitrification rate is inhibited by the high temperature, so the relationship no longer holds. Figure 3-14 illustrates the effect of temperature on nitrification and shows that the rate rapidly decreases at temperatures beyond 30°C.

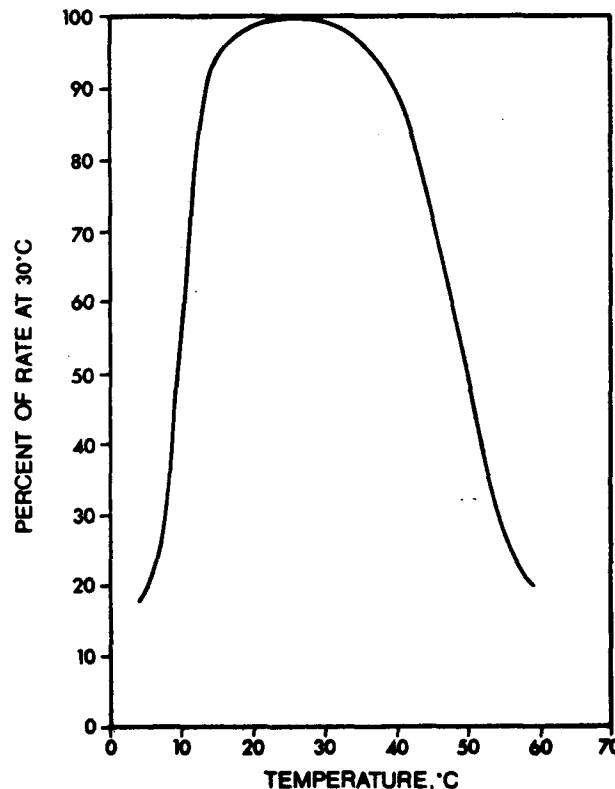
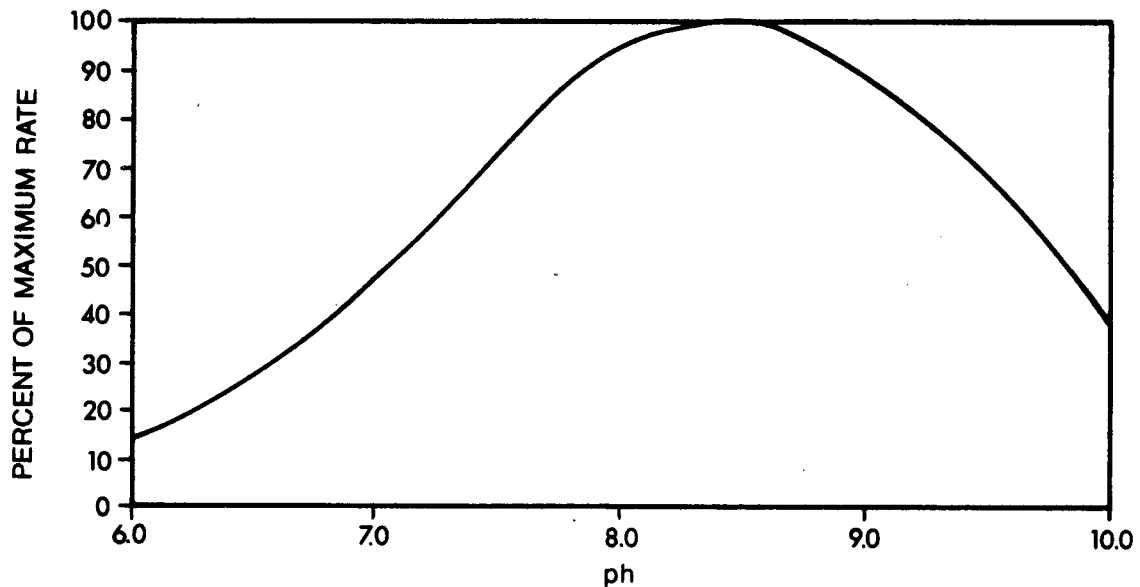


Figure 3-14. Effect of Temperature on Nitrification as Reported by Borchardt (1966).

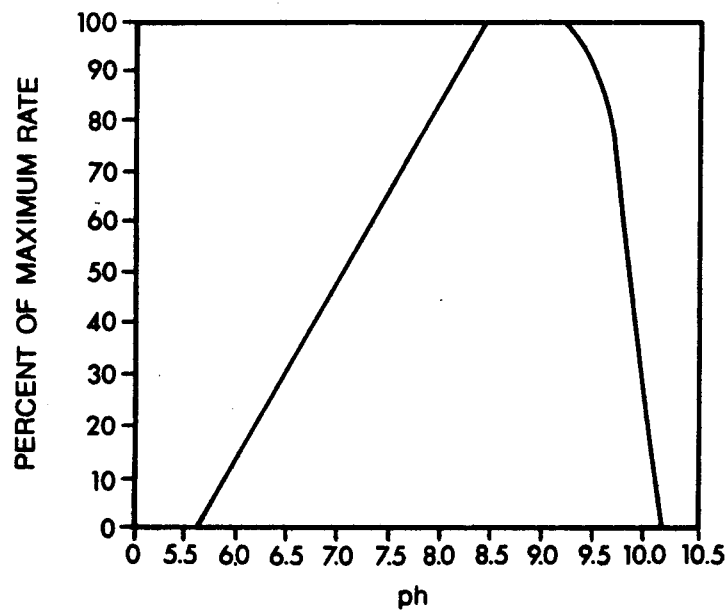
The influence of pH on rates of nitrification is also quite important. If pH is outside of the range 7.0 to 9.8, significant reduction in nitrification rates can occur. Table 3-19 indicated that the optimal pH for nitrification is approximately 8.5 and at pH values below about 6.0, nitrification is not expected to occur. Figure 3-15 shows the effect of pH

on ammonia and nitrite oxidation. A more thorough review of pH effects is contained in Sharma and Ahlert (1977).

Effects of solid surfaces have frequently been documented as being important for nitrification (e.g., Kholdebarin and Oertli, 1977). The following section discusses this effect more fully through a number of case studies.



(a) AMMONIA OXIDATION (Wild et.al.,1971)



(b) NITRITE OXIDATION (Myerhof,1916)

Figure 3-15. pH Dependence of Nitrification.

3.4.4 Case Studies and Nitrification Rates

Table 3-21 summaries case studies of nitrification in natural waters. These studies are intended to show how various researchers have determined nitrification rates in natural waters, some of the complications that can occur in doing so, and what the rates are.

Except for Slayton and Trovato (1978, 1979) all the case studies are for streams or rivers. Note the high variability in nitrification rates from study to study. For rivers, documented first order nitrification rates varied from 0.0/day to 9.0/day. For the two Potomac estuary studies, the nitrification rates were fairly small and constant (0.1 to 0.14/day). The nitrification rate was often determined from plots of TKN or NBOD versus distance or travel time. Figure 3-16 shows an example. A number of the studies (e.g., Koltz (1982) and Ruane and Krenkel (1978)) emphasized that algal uptake of ammonia can be an important transformation and should be accounted for in the rate determination. The increase of nitrate nitrogen can be monitored, as well as the decrease in ammonia nitrogen for more conclusive evidence that nitrification is occurring. Bingham et al. (1984) show how the nitrification rate constant is changed in a QUAL-II application when algae is simulated compared to when algae is not simulated.

Several of the case studies have enumerated nitrifying bacteria present in the water column and in the sediments (e.g., Kreutzberger and Francisco (1977)). Far more nitrifying organisms are typically present in the sediments than in the water column. Case studies on the following rivers have reached the same conclusion:

- Kanawha River, West Virginia (U.S. EPA, 1975)
- Tame and Trent Rivers, England (Curtis et al., 1975)
- North Buffalo Creek, North Carolina (Williams and Lewis, 1984)
- Willamette River, Oregon (Rinella et al., 1981)
- Chattahoochee River, Georgia (Jobson, undated)

TABLE 3-21. CASE STUDIES OF NITRIFICATION IN NATURAL WATERS

Reference	Study Area	Purpose of Study	Reported Nitrification Rates	Methods of Determining Nitrification Rates	Comments
Wezernak and Gannon (1968) Stratton and McCarty (1969) Blain (1969)	Clinton River, Michigan, a shallow stream with velocities of 1-2 fps	To mathematically model nitrification in a stream (This was one of the earlier modeling attempts)	ammonia oxidation: 3.1-6.2/day nitrite oxidation: 4.3-6.6/day	Measurements of ammonia, nitrite, and nitrate at three locations within the stream	The nitrogen balance developed indicated that nitrification was primary mechanism responsible for observed nitrogen transformations.
Gowda (1983)	Speed River, Canada, a relatively shallow river with velocities from 0.3 to 1.5 fps	To determine the affects of nitrification on dissolved oxygen levels within the river	0.2-4.41/day	Plots of TKN versus travel time	NBOD predicted to be much more important on the dissolved oxygen deficit than CBOD.
Curtis (1983)	Still River, Connecticut	To determine the fate of ammonia in the river by simulating oxidative and non-oxidative transformations	0.0-0.4/day	Comparison of total ammonia decrease to nitrate increase	
Deb and Bowers (1983)	South Fork of Shenandoah River	To simulate the dissolved oxygen of the river using the DIURNAL model	0.2-1.25/day	Plots of NBOD versus travel time	
Deb, Klafner-Snyder, and Richards (1983)	Leatherwood, Creek, Arkansas	To simulate the dissolved oxygen dynamics of a small surface-active stream for wasteload allocation purposes	1.1-7.1/day	Plots of TKN versus travel time	
Ruane and Krenkel (1978)	Holston River, Tennessee	To examine the various nitrogen transformations that occur in the river	0.15-0.3/day	Rate of ammonia reduction and rate of nitrate increase	The complexity of the nitrogen cycle in the Holston River is discussed including the effects of ammonia transformations other than caused by nitrification.
Koltz (1982)	Iowa and Cedar Rivers, Iowa	To determine the locations and rates of nitrification downstream from two wastewater treatment plants	0.5-9.0/day	Rate of ammonia reduction and rate of nitrate increase	Algal assimilation of ammonia appeared to be an important transformation process. Laboratory rates of nitrification varied from 0.02-0.35/day.

(continued)

TABLE 3-21. (continued)

Reference	Study Area	Purpose of Study	Reported Nitrification Rates	Methods of Determining Nitrification Rates	Comments
Kreutzberger and Francisco (1977)	Morgan Creek, Ruin Creek, and Little Lick Creek; three shallow streams in North Carolina	To determine the distributions of nitrifying organisms, and to examine the nitrogen transformation occurring in the streams	-	-	Counts of nitrifying organisms were enumerated in the water column and in the top 1 cm of sediments. The populations were much larger in the sediments, which indicated that nitrifica- tion was occurring predominantly in the sediments and not in water column.
Cirello et al. (1979)	Passaic River, New Jersey	To determine whether nitrification was a significant process in the Passaic River	-	-	There were high ammonia nitrogen concentrations in the river with relatively little nitrification occurring. The potential for nitrification appeared high, and was expected to be exerted if water quality within the river improved.
Finsten and Matulewicz (1974)	Passaic River, New Jersey	To determine the distribution of nitrifying bacteria in the river	-	-	Nitrifying bacteria were found to be from 21 to 140,000 times more abundant volumetrically in sedi- ments than in the water column.
Slayton and Trovato (1978, 1979)	Potomac Estuary	To determine factors important in the oxygen balance within the estuary	0.10-0.14/day	Thomas Graphical Method	-

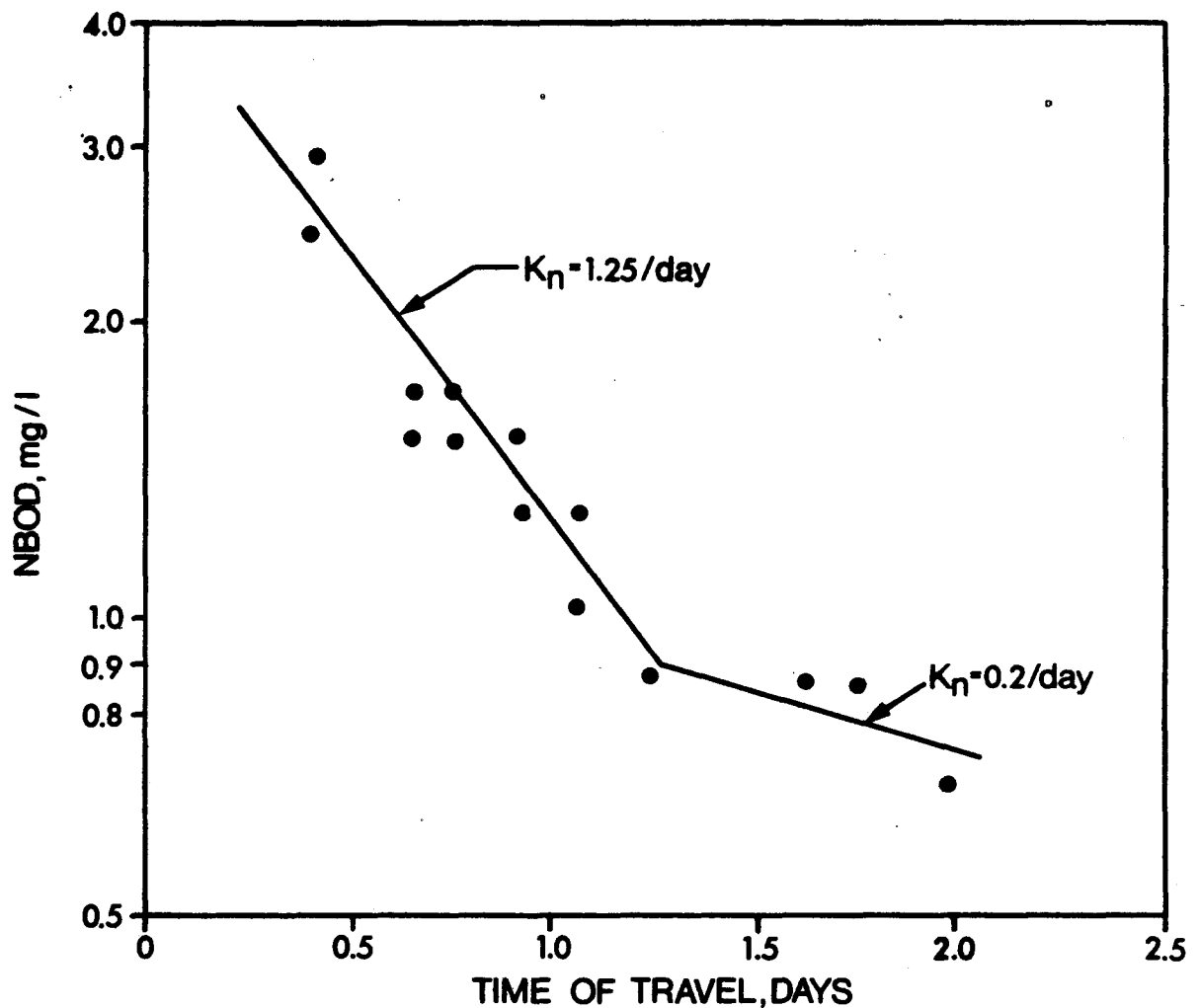


Figure 3-16. Nitrogenous biochemical oxygen demand versus travel time in Shenandoah River (Deb and Bowers, 1983).

Additional nitrification rates are shown in Table 3-22. Bansal (1976) has documented nitrification rates in numerous rivers throughout the United States, and developed a method to predict nitrification rate based on hydraulic data. His method has been criticized by Gujer (1977) and Brosman (1977) and is not reported.

Relatively few nitrification rates were found for lakes or estuaries. The few data in Table 3-22 for lakes and estuaries are generally in the range 0.1/day to 0.5/day.

TABLE 3-22. SUMMARY OF NITRIFICATION RATES

River	Maximum	Average	Minimum	Reference
Grand River, Michigan	3.9	2.6	1.9	Courchaine (1968)
Clinton River, Michigan	15.8 4.0	5.7 1.9	2.2 0.4	Wezernak and Gannon (1968)
Truckee River, Nevada	2.4	1.9	--	O'Connell and Thomas (1965)
South Chickamauga Creek, Tennessee	1.9	--	1.1	Tennessee Valley Authority Ruane and Krenkel (1978)
Oostanaula Creek, Tennessee	0.8	--	0.1	Tennessee Valley Authority Ruane and Krenkel (1978)
Town Branch, Alabama	--	0.7	--	Tennessee Valley Authority Ruane and Krenkel (1978)
Chattahoochee River, Georgia	--	0.44	--	Stamer <u>et al.</u> (1979)
Willamette River, Oregon	0.7	--	0.4	Rinella <u>et al.</u> (1981)
Flint River, Michigan	2.5	1.4	0.1	Bansal (1976)
Upper Mohawk River, New York	0.3	0.25	0.25	Bansal (1976)
Lower Mohawk River, New York	0.3	0.3	0.3	Bansal (1976)
Barge Canal near Upper Mohawk River, New York	0.25	0.25	0.25	Bansal (1976)
Ohio River	0.25	0.25	0.25	Bansal (1976)
Big Blue River, Nebraska	0.25	0.11	0.03	Bansal (1976)
Delaware River Estuary	0.54	0.3	0.09	Bansal (1976)
Willamette River, Oregon	--	0.75* 1.05**	--	Alvarez-Montalvo, <u>et al.</u> undated
Ouachita River, Arkansas and Louisiana	--	0.1* 0.5**	--	NCASI (1982c)
Potomac Estuary	--	0.09-0.13	--	Thomann and Fitzpatrick, 1982
Lake Huron and Saginaw Bay	--	0.20	--	Di Toro and Matystik, 1980
New York Bight	--	0.025	--	O'Connor <u>et al.</u> 1981

Note: Nitrification rates are in units of 1/day.

* Ammonia Oxidation

** Nitrite Oxidation

3.4.5 Summary

Typically modelers simulate nitrification by first order kinetics, either the single stage or two stage approach. Most nitrification rate data have been collected in streams and rivers, where the rates can be quite variable due to bottom effects. Instream rates can differ significantly from laboratory or bottle rates. However, for large bodies of water (typically lakes or estuaries) the relative importance of the bottom is diminished, and nitrification rates tend to approach bottle rates. Available data suggest nitrification rates between 0.1 to 0.3/day are often appropriate for large lakes, large rivers, or estuaries.

In flowing waters, instream nitrification rates are often determined based on TKN versus travel time. Care should be taken that the assumptions of the approach are met, and that processes that transform nitrogen other than nitrification are assessed (i.e., the other components of the nitrogen cycle).

Because benthic nitrification can be important in small streams, it is important not to "doubly count" oxygen sinks in modeling applications. A component of the sediment oxygen demand would include benthic nitrification, so the two processes need to be accounted for in a mutually exclusive way for modeling applications.

Very few studies actually try to measure populations of nitrifiers in natural systems. This, however, is the most conclusive method to confirm that nitrification is occurring.

3.5 SEDIMENT OXYGEN DEMAND (SOD)

3.5.1 Concept of SOD

Oxygen demand by benthic sediments and organisms can represent a large fraction of oxygen consumption in surface waters. Benthic deposits at any given location in an aquatic system are the result of the transportation and

deposition of organic material. The material may be from a source outside the system such as leaf litter or wastewater particulate BOD (allochthonous material), or it may be generated inside the system as occurs with plant growth (autochthonous material). In either case, such organic matter can exert a high oxygen demand under some circumstances. In addition to oxygen demand caused by decay of organic matter, resident invertebrates can generate significant oxygen demand through respiration (Walker and Snodgrass, 1984). The importance of this process to water quality modeling is reflected in a recent symposium (Hatcher and Hicks, 1984). This same symposium also reviewed measurement techniques and a consensus favoring in situ measurement was reached.

It is generally agreed (e.g., Martin and Bella, 1971) that the organic matter oxygen demand is influenced by two different phenomena. The first is the rate at which oxygen diffuses into the bottom sediments and is then consumed. The second is essentially the rate at which reduced organic substances are conveyed into the water column, and are then oxidized. Traditional measurement techniques, whether they are performed in situ or in the laboratory, do not differentiate between the two processes but measure, either directly or indirectly, the gross oxygen uptake. Hence, in modeling dissolved oxygen, a single term in the dissolved oxygen mass balance formulation is normally used for both processes. If the two phenomena are modeled separately (e.g., see Di Toro, 1984), then additional modeling complexity is necessary.

The process is usually referred to as sediment oxygen demand (SOD) because of the typical mode of measurement: enclosing the sediments in a chamber and measuring the change in dissolved oxygen concentration at several time increments. This technique is used in the laboratory or in situ. The oxygen utilized per unit area and time ($\text{gO}_2/\text{m}^2\text{-day}$) is the SOD. The technique measures oxygen consumption by all of the processes enclosed in the chamber: chemical reactions, bacterially mediated redox reactions, and respiration by higher organisms (e.g., benthic worms, insects, and molluscs). Background water column respiration is then subtracted from this rate to compute the component due solely to the

sediment interface. SOD is usually assumed to encompass the flux of dissolved constituents such as DO to sediment and reduced chemicals to the water column. However, solid particle flux as BOD or sediment entrainment or settling is modeled separately.

The major factors affecting SOD are: temperature, oxygen concentration at the sediment water interface (available oxygen), makeup of the biological community, organic and physical characteristics of the sediment, current velocity over the sediments, and chemistry of the interstitial water. Each of these factors is a resultant of other interacting processes occurring elsewhere in the aquatic system. For example, temperature and available oxygen can be changed as a result of transport and biochemical processes in the water column or system boundaries. Temperature and oxygen are usually modeled explicitly, and can be used as input variables to the SOD process equations. Another important linkage is that the biological community will change with the water quality (e.g., oxygen and nutrient concentrations) and productivity of the system. The organic characteristics will change over the long term due to settling of organic matter (detritus, fecal matter, phytoplankton) and its subsequent degradation and/or burial by continued sedimentation. The biological community and the organic and physical characteristics of the bottom sediments are usually treated as a composite characteristic of the particular system. Recently, techniques have been developed for investigating these factors; however, the usual technique is to measure the SOD directly rather than the underlying factors that control the processes of SOD.

At least two major factors affecting SOD are usually neglected in SOD modeling. Current velocity is often neglected despite the fact that it has a major effect on the diffusive gradient of oxygen beginning just below the sediment-water interface. Most measurement techniques provide mixing by internal mixing or by recirculating or flow-through systems to minimize the effect of concentration gradients. However, the velocity of such systems may be insufficient (Whittemore, 1984a) or may be so vigorous as to cause scour and resuspension. Interstitial water chemistry affects substrates for biochemical and non-biochemical oxidation-reduction reactions and their

reaction rates. This factor is also usually neglected in SOD measurements and kinetic formulations.

3.5.2 Kinetics

The generalized equation for sediment oxygen demand is:

$$\frac{dC}{dt} = \frac{-SOD}{H} = f(\text{dissolved oxygen, temperature, organisms, substrate}) \quad (3-51)$$

where H = water depth, m

SOD = sediment oxygen demand (as measured), $gO_2/m^2\text{-day}$

t = time

C = oxygen concentration in the overlying water, mg/l

3.5.2.1 Dissolved Oxygen

The benthic oxygen consumption has been hypothesized to depend on the dissolved oxygen concentration in the overlying waters (e.g., Edwards and Rolley, 1965; McDonnell and Hall, 1969):

$$SOD = a C^b \quad (3-52)$$

where a,b = empirically determined constants

In the McDonnell and Hall (1969) study, b was found to be 0.30 and a to vary from 0.09 to 0.16, primarily as a function of the population density of benthic invertebrates.

Lam et al. (1984) use a Michaelis-Menten relationship to express the effects of oxygen on SOD:

$$\frac{dC}{dt} = - \frac{k_s A_s}{V} \frac{C}{K_{O_2} + C} \quad (3-53)$$

where k_s = rate constant for SOD in Lake Erie, $0.1 \text{ g O}_2/\text{m}^2\text{-day}$
 A_s = area of the sediment, m^2
 V = volume of water layer, m^3
 K_{O_2} = oxygen half saturation constant (1.4 mg/l)
 C = oxygen concentration, mg/l

Walker and Snodgrass (1984) divided SOD in Hamilton Bay in Lake Ontario into two fractions: chemical-microbial (CSOD) and biological (BSOD). The chemical fraction was defined as a first-order function of oxygen:

$$\text{CSOD} = k_1(T) C \quad (3-54)$$

where $k_1(T)$ = temperature-adjusted rate constant for biochemical SOD,
 $1/\text{day}$

The biological fraction was estimated to be 20-40 percent due to macroinvertebrates in Hamilton Bay sediments but still followed a Michaelis-Menten relationship:

$$\text{BSOD} = u(T) \frac{C}{K_{O_2} + C} \quad (3-55)$$

where $u(T)$ = temperature-adjusted rate constant for biological SOD
 (obtained by measurement: range = 0.58 to $5.52 \text{ g O}_2/\text{m}^2\text{-day}$), $1/\text{day}$

K_{O_2} = oxygen half-saturation constant (1.4 mg/l)

It is interesting to note the similarity between the two estimates of K_{O_2} (Lam et al., 1984; Walker and Snodgrass, 1984).

The direct effects of dissolved oxygen on the rate constant are generally neglected except in a few models. For example, in the HSPF model (Johansen et al., 1981), dissolved oxygen concentration affects the rate of sediment oxygen utilization exponentially:

$$\frac{dC}{dt} = -\frac{k_T}{H} (1 - e^{-1.22 C}) \quad (3-56)$$

where k_T = the temperature adjusted rate constant, $\text{mg/m}^2\text{-day}$

3.5.2.2 Temperature

Temperature effects on SOD are most commonly modeled using the van't Hoff form of the Arrhenius relationship:

$$k_T = k_{Tr} \theta^{(T-Tr)} \quad (3-57)$$

where k_T = the rate at ambient temperature T

k_{Tr} = the rate at a reference temperature (usually $Tr=20^\circ\text{C}$)

θ = the temperature coefficient for adjusting the rate
(Table 3-23)

Although this form of the relationship is the most common and gives equivalent results to the Arrhenius equation, it is not preferred in standard nomenclature (Grau et al., 1982).

The exceptions to use of Equation (3-57) are RECEIV-II (Raytheon, 1974), HSPF (Johanson et al., 1981), and SSAM-IV (Grenney and Kraszewski, 1981). RECEIV-II apparently does not provide a temperature correction for the SOD rate coefficient although other rate coefficients in the model are adjusted according to Equation (3-57) with $\theta = 1.047$ for CBOD. HSPF uses a linear function for adjusting the SOD for temperature:

$$k_T = 0.05 T_w k_{20} \quad (3-58)$$

where k_T = the temperature adjusted coefficient

k_{20} = the rate constant at 20°C

T_w = water temperature, $^\circ\text{C}$

TABLE 3-23. SOME TYPICAL VALUES OF THE TEMPERATURE COEFFICIENT
FOR SOD RATE COEFFICIENTS USED IN WATER QUALITY MODELS

Model	θ	Q10(20°C)*	Reference
DOSAG-3	1.047	1.58	Duke & Masch (1973)
QUAL-II	1.047	1.58	Roesner <u>et al.</u> (1977)
Vermont QUALII	1.047	1.58	JRB (1983)
Lake Erie Model	1.08	2.16	Di Toro & Connolly (1980)
WASP	1.08	2.16	Thomann & Fitzpatrick (1982)
WASP	1.1	2.59	O'Connor <u>et al.</u> (1981)
LAKECO	1.02	1.22	Chen & Orlob (1972, 1975)
WQRRS	1.02-1.04	1.22-1.48	Smith (1978)
ESTECO	1.02-1.04	1.22-1.48	Brandes (1976)
DEM	1.04	1.48	Genet <u>et al.</u> (1974)
EAM	1.02	1.22	Bowie <u>et al.</u> (1980)
EAM	1.047	1.58	Tetra Tech (1980), Porcella <u>et al.</u> (1983)
USGS-Steady	1.065	1.88	Bauer <u>et al.</u> (1979)
AQUA-IV	1.02-1.09	1.22	Baca & Arnett (1976)
EXPLORE-I	1.05	1.63	Baca <u>et al.</u> (1973)
Laboratory/Field Studies	1.040-1.130	1.5-3.4	Zison <u>et al.</u> (1978); Whittemore (1984b)

* Q10(20°C) = ratio of k_2/k_1 at $k_2/k_1 = \theta^{10}$.

Grenney and Kraszewski (1981) used a modification of the Thornton and Lessem (1978) equation for SSAM-IV to provide, essentially, a continuously variable adjustment coefficient (θ) for the rate constants in biological processes. The equation adjusts over a temperature range of 5 to 30°C which is similar to using Equation (3-51) with a variable θ coefficient:

$$\tau_{11} = N \frac{K_1 e^{\gamma(T-T_1)}}{1-K_1(1-e^{\gamma(T-T_1)})} \quad (3-59)$$

where τ_{11} = a multiplier applied to the rate at the optimum temperature, dimensionless

N = an adjustment coefficient for rate processes, dimensionless

K_1 = reaction rate multiplier near lower threshold temperature, 1/day

γ = specific rate coefficient, 1/°C

T = environmental temperature, °C

T_1 = lower threshold temperature, °C

The coefficient τ_{11} is multiplied times the SOD (or benthic loading rate) directly in SSAM-IV.

Although many models use the same formulation (Equation (3-57)) of the temperature correction equation for the SOD rate constant, the value of the constant θ is in dispute. Whittemore (1984b) reviewed literature values as well as his laboratory values in an attempt to determine measurement uncertainty. For analysis of his data, Whittemore chose $\theta = 1.08$ with an estimate of uncertainty of ± 0.01 . Then performing a sensitivity analysis for the range of $\theta = 1.07-1.09$ (1.08 ± 0.01), Whittemore showed that SOD would increase 12 percent when θ is increased by 0.01 for a temperature range of 12°C (20 to 32°C). He cautions that complete physical, chemical, and biological descriptions of SOD measurements are needed, both for in situ and studies measurements. Even in his own studies where a single method was used, the measured mean SOD using a stirred in situ respirometer had a standard deviation of 44 percent of the mean (Whittemore, 1984b).

Additional field experience and the use of divers to place the respirometers should measurably improve these results.

3.5.2.3 Biological Effects on SOD

The biological component is usually neglected when modeling SOD, because of the complexity of modeling benthic microorganisms and macroinvertebrates. The spatial and seasonal variability in SOD caused by sediment biological processes and communities results in variation in SOD that modelers appear to account for by varying the temperature coefficient. Some investigators have attempted to incorporate this variation directly in the model (Grenney and Kraszewski, 1981), or have suggested that the value of the temperature coefficient changes with season (e.g., Bradshaw *et al.*, 1984) or with location downstream (e.g., Mancini *et al.*, 1984). Other models (LAKECO, ESTECO, WQRRS, EAM) incorporate a benthic organisms compartment and may be able to evaluate the effects of benthos on SOD directly. However, no verification studies have been discovered that demonstrate this to be a useful technique.

3.5.2.4 Substrate Variability

The process describing the substrate utilized is where most models differ (Table 3-24). In the first water quality models that were widely used (DOSAG-3, QUAL-II), the decay of substrate is assumed to balance continued settling resulting in a steady-state sediment concentration of oxygen-demanding substrate. The resulting equation is:

$$\frac{dC}{dt} = -k_T/H, \quad (3-60)$$

where k_T = temperature adjusted rate constant SOD, gO_2/m^2 -day
 H = mean water depth, m

As shown in Table 3-24, most models have followed this approach.

TABLE 3-24. MODEL FORMULATIONS COMMONLY USED IN SOD COMPUTATIONS

Formulation	Units	Description	Model (Reference)
k/A	k,mgO ₂ /m day A,m ²	SOD rate normalized by bottom area	DOSAG-3 (Duke & Masch, 1973) QUAL-II (Roesner <u>et al.</u> (1977)
k/H	k,mgO ₂ /m ² day H,m	SOD rate normalized by mean depth	Vermont QUAL-II (JRB, 1983) USGS-Steady (Bauer <u>et al.</u> 1979) AQUA-IV (Baca & Arnett, 1976) WASP (O'Connor <u>et al.</u> 1981) RECEIV-II (Raytheon, 1974) DEM (Genet <u>et al.</u> 1974) HSPF (Johanson <u>et al.</u> 1981)
a k SED	a,mgO ₂ /mg Sed k,l/day SED, mg Sed/m ³	Conversion factor Decay rate Sediment areal concentration	LAKECO* (Chen & Orlob, 1972, 1975) WQRRS* (Smith, 1978) EAM* (Bowie <u>et al.</u> , 1980; Tetra Tech, 1980; Porcella <u>et al.</u> , 1983) EXPLORE-I (Baca <u>et al.</u> , 1973)

*NOTE: Additional SOD occurs due to respiration by the benthic organism compartment, which is modeled separately from sediment oxygen demand.

Substrate has been incorporated directly into ESTECO, LAKECO, WQRRS, EAM, and EXPLORE-I. Different settling rates of oxygen-demanding organic materials can lead to different amounts of sediment materials, and consequently different SOD rates calculated according to:

$$\frac{dC}{dt} = - a k \text{ SED} \quad (3-61)$$

where a = stoichiometric conversion factor relating oxygen to organic sediment, $\text{mg O}_2/\text{mg sediment}$

k = sediment decay rate constant, $1/\text{day}$

SED = sediment substrate that is subject to decay

In EXPLORE-I, only carbonaceous BOD is simulated as the substrate (SED), which in turn is affected by scour or settling from the water column. In the other models, all of the nutrient elements (C, N, P) are transformed according to a first-order reaction ($k \text{ SED}$) but sediment oxygen demand is exerted only by carbon. Values of the conversion factor for sedimented organic carbon to O_2 lie in the range of 1.2 to 2.0 $\text{mgO}_2/\text{mg sediment}$. Nitrogen decays to ammonium and is released to the overlying waters where nitrification can take place (see Section 3.4). Other nutrients also enter the overlying waters as a result of similar transformations.

In some versions of the WASP model (Di Toro and Connolly, 1980; Thomann and Fitzpatrick, 1982), the oxygen-demanding materials in the sediment are divided into multiple compartments. First, the decay processes of sediment organic matter generate concentrations of CBOD and NBOD constituents in interstitial waters. Then both CBOD and NBOD are released to the water column where they subsequently decay in the appropriate compartments. In addition to CBOD release, oxygen utilization in the interstitial water is computed as oxygen equivalents, and diffusion into the interstitial water compartment is determined. If oxidation in excess of the amount available from diffusion occurs, these excess "oxygen equivalents" continue to represent a potential demand on the dissolved oxygen system. Finally, a deep oxygen demand has been hypothesized in an attempt to account for the measured oxygen demand. These concepts are described Di Toro and Connolly,

1980. More recently, Di Toro (1984) has provided an additional correction to SOD from denitrification of nitrate, although he suggests that this correction is usually negligible.

3.5.3 Measurement Techniques

Essentially three types of measurement techniques have been used to estimate SOD rates: model calibration to estimate SOD, in situ measurements using respiration chambers, and laboratory respiration chamber measurement using cores or dredged samples. However, all three methods have severe disadvantages and the uncertainty of calculating SOD rates is so great that the simple formulations in the model equations (Table 3-24) are very appealing to model users. Unfortunately, these simple formulations will not result in credible models with good predictive capability when single values are used for rates and coefficients.

It would be expected that considerable spatial and temporal variation would occur in SOD. Spatially, the bed sediments of streams, lakes, and estuaries vary in their physical and chemical characteristics, rates of deposition, and other factors. For example, a stream may have fine sediments in low velocity areas and coarse cobble or boulders in steep gradient-high velocity reaches. Depth and velocity can vary significantly in any one cross-section. Reservoirs have deposition zones near inlets and at dam structures. Estuaries like streams and lakes vary considerably in substrate type and water velocity but are influenced by the salinity gradient and an added factor of coagulation and rapid settling in zones where fresh and saline waters mix.

Another source of variation is temperature. Temperature varies seasonally but that is accounted for in use of the van't Hoff or similar relationships. However, temperature and season both cause a shift in benthic community composition. Macroinvertebrate populations, especially emergent insects, change dramatically with life stage. Also, it would be expected that considerable variation in microbial community characteristics would occur in response to temperature changes.

These spatial and seasonal characteristics suggest that a large number of SOD measurements would be required to estimate and obtain sufficient variation in rate coefficients. This has led to the development of in situ and laboratory methods for measuring SOD that will be site-specific and seasonal for SOD. SOD mapping strategies may be necessary. Ideally, in situ methods would provide the best approach, but considerable variation in results occurs because of problems associated with field sampling:

- Horizontal and longitudinal non-homogeneity of stream bottom materials. Areas of cobble, soft sediments, logs, and bedrock, increase the cost of measurement because more samples are needed. Soft, flocculent sediments are very difficult to evaluate with in situ methods. In some streams, an inaccurate characterization of reach-averaged SOD will be obtained.
- Difficulties in placement of respiration chamber. For example, obtaining a complete seal in cobbled and bouldered areas or where significant interaction with the ground water system occurs is essentially impossible.
- Mixing in the respiration chamber may not be modeled correctly nor simulate natural conditions and this is reflected in the wide variance in results from measurements. For example, the Institute of Paper Chemistry reported on a comparison of 5 in situ samplers of two basic types (recirculating and internally mixed) and found the results to be markedly different (Parker, 1977).

Laboratory measurements suffer from similar problems. They would appear to work reasonably well for aquatic systems of relatively uniform sediment characteristics, but heterogeneous sediments often lead to measurement variability.

Some practices improve laboratory measurement: correcting of results for varying sediment depth is usually unnecessary when depths exceed 5-10 cm; undisturbed core samples are preferred over dredge samples even though they are more costly to collect; storage of samples and acclimation of samples to laboratory temperatures is discouraged because of potential changes in benthos or substrate; divers may help to improve precision.

In regard to the effect of variability in oxygen-demanding materials, there appears to be no strong relationship between SOD and various measures of organic matter (NCASI, 1978), but this may have been due to inaccurate measurement techniques. Improper mixing (i.e, velocity too high or too low), inadequate oxygen supply, storage or improper pretreatment of samples in the laboratory, and inappropriate laboratory temperatures may lead to errors that prevent the derivation of SOD/substrate relationships. However, Gardiner et al. (1984), using a laboratory chamber, showed that SOD was related to chemical oxygen demand (COD) of the sediments in Green Bay, a large gulf in the northwest corner of Lake Michigan, according to the following equation:

$$\text{SOD} = 7.66 \text{ COD} / (156.5 + \text{COD}) \quad (3-62)$$

As further evidence, the higher SOD values coincided with areas of summer dissolved oxygen depletion in Green Bay.

Given the many sources of measurement error, it is not surprising that Whittemore (1984b) was unable to correlate literature SOD values obtained in simultaneous field and laboratory measurements. He obtained a low r^2 value of 0.58. But even more significant, the in situ SOD values were consistently higher than laboratory derived values at low SOD concentrations and the reverse observed at high SOD concentrations. This systematic error indicates the need for better methods of estimating SOD as well as developing a better understanding of the component SOD mechanisms.

The model calibration approach to estimating SOD is essentially a determination of the SOD rate by calibration subject to the constraint of a

reasonable range of SOD values. Thomann (1972) used literature SOD rates and modeling experience to suggest SOD ranges for certain environments (Table 3-25). The model approach (e.g., Terry and Morris, 1984; Draper et al., 1984), by itself, contains considerable variance because there are uncertainties in the other processes (reaeration, nitrification, respiration, photosynthesis, flow) as well as the considerable spatial and temporal variation expected in most aquatic environments. Lam et al. (1984) suggest that variation in dissolved oxygen load to Lake Erie owing to

TABLE 3-25. AVERAGE VALUES OF OXYGEN UPTAKE RATES OF RIVER BOTTOMS (AFTER THOMANN, 1972)

Bottom Type and Location	Uptake (g O ₂ /m ² -day) @ 20°C	
	Range	Average
<u>Sphaerotilus</u> - (10 gm dry wt/m ²)	-	7
Municipal Sewage Sludge- Outfall Vicinity	2-10.0	4
Municipal Sewage Sludge- "Aged" Downstream of Outfall	1-2	1.5
Estuarine mud	1-2	1.5
Sandy bottom	0.2-1.0	0.5
Mineral soils	0.05-0.1	0.07

hydrologic fluctuations could easily mask the effects of SOD on water column oxygen.

3.5.4 Summary

There is a diversity of modeling and measurement techniques used for predicting oxygen consumption by sediments. This diversity reflects the need for better process descriptions and measurement techniques. Simple zero-order model formulations have been used, but first-order multi-component reactions with a separate benthic organism component may be needed to accurately model sediment oxygen demand (SOD).